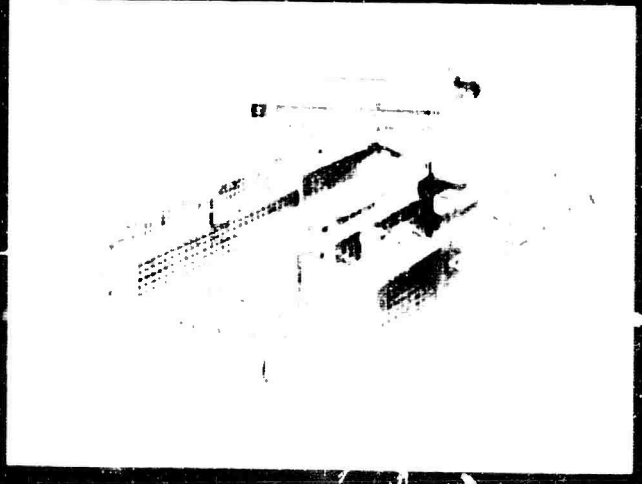

BAUSCH & LOMB INCORPORATED

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STUDY OF NON-OXIDE MATERIALS WITH DEFECT STRUCTURES

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Contract No.	NOnr 3632(00)
Task No.	NR 015-501
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Contractor	Bausch & Lomb Incorporated Rochester, New York 14602
Date of Contract	27 Oc ber 1961
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Final Summary Report

Prepared by: P. C. Velasquez and H. C. Hafner

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APPENDICES

A B S T R A C T

Several ionic fluoride systems, demonstrating the feasibility of preparing materials with controllable defects up to 20 mole %, have been investigated. Methods of preparation are described. The materials were characterized with respect to type of defect present and its influence on the properties of the host structure. A significant new contribution to the literature was the discovery of extensive defect concentration in the tysonite structure and establishment of the defect model as predominantly anion vacancies. Hot-pressed specimens exhibit ionic conduction considerably greater than the non-defect tysonite and other hot-pressed fluorides.

A tetragonal phase, heretofore unreported, was found in the system $KMgF_3$-ScF_3.

Major problems encountered were oxidation and accomplishing homogeneity in the solid solutions.

Polycrystalline compacts of these materials were fabricated using hot-pressing apparatus and techniques developed for this purpose. Observed alteration of the refractive index, unit cell size, and density of a material related to a change in type and concentration of defect, and successful compaction of polycrystalline aggregates, demonstrates the feasibility of predicting and tailor-making materials having desired properties.

I. INTRODUCTION

Statement of Work:

This study was undertaken to evaluate and prepare new fluorides expected to possess controllable gross defects, to determine their physical properties especially as a function of the amount and nature of the defect, and to fabricate polycrystalline aggregates of the materials under high pressure and temperature conditions and perform an intensive study of their mechanical, optical, and electrical properties.

Background, Scope, Objectives:

It has become generally recognized that the most pure and perfect of crystalline solids is never, in practice, perfect. Rather all substances are defective in some way.

The effects of these defects, existing in concentrations on the order of parts per million, on the properties and behavior of semi-conductor materials are legion.

However, it has not been fully appreciated that some crystalline substances can tolerate extreme lattice perturbations, well beyond the parts per million range. More importantly--although material studies, notably in the crystal-chemical and related fields, have brought forth observations and established principles governing the occurrence of these non-ideal crystals--there has been little systematic effort to determine the changes in physical properties of such defective materials in relation to the amount and type of lattice defect.

This study attempted to demonstrate certain general types of "gross" defects, and was aimed at determining the effect of defect type and concentration on various physical properties of materials. The results may be useful as an approach to controlling specific properties of materials by a chemical control over defects.

"Gross" defects were conveniently defined as those existing in concentrations of several percent, in contrast to the more familiar consideration of lattice defects in the parts per million range.

The following list summarizes the types of defects expected to occur.

	Type	System
1.	Substitutional - A cation replaces ionic species of comparable size and charge in the best lattice.	$M_I^{2+}F_2$-($M_{II}^{2+}F_2$)

	Type	System
2.	Interstitial - Electrical neutrality is maintained by filling lattice interstices with ionic species to compensate for increased charge at neighboring lattice sites.	$M^{2+}F_2$-($M^{3+}F_3$)
3.	Cation Vacancy - A higher charge cation proxies for a lower valence cation, with electrical neutrality maintained by omission of cations at a different site.	$M^{2+}F_2$-($M^{3+}F_3$)
4.	Anion Vacancy - Anions are omitted in the host structure to compensate for lower cation charges.	$M^{3+}F_3$-($M^{2+}F_2$)

The study program was divided into three general phases, as follows:

1. A survey of systems likely to demonstrate the various defect types.

2. The selection of representative systems and detailed characterization of the defect structure.

3. Preparation of hot-pressed polycrystalline aggregates of the selected materials and physical property correlation with defect type and amount.

Several factors influenced the selection of fluoride systems for this study. With fluorides, the well-known oxide structures could be easily imitated at lower temperatures. Furthermore, they comprise a class of compounds possessing valuable infra red transmitting properties. Finally, since considerably less work has been done on fluorides than oxides, worthwhile contributions to the field were anticipated.

Since we have had extensive experience with hot pressing techniques[1], the fabrication of polycrystalline specimens via this mode was emphasized.

[1] Bibliography, (1), (20)

II. EQUIPMENT AND MATERIALS

Aside from the conventional laboratory facilities, the following items warrant special mention:

Reaction Furnaces:

A Marshall type, 1200°C, vertical tube furnace was used for the initial accumulation of time-temperature-composition data. This furnace is described in detail in an earlier annual report[1].

A Glo-bar furnace was constructed for use with reactions exceeding 1200°C. This furnace, capable of heating reaction mixtures up to 1400°C under a controlled atmosphere, also is described in detail in a previous report[2].

A Harper Glo-bar type glass melting furnace with controlled atmosphere capabilities was used to react pound-lot quantities of the selected materials.

Hot-Pressing Apparatus:

A sketch and a detailed description of the hot-pressing apparatus has been given in a previous report[3]. The sketch has been included in the Appendix, E. Briefly, it had capabilities up to 50,000 psi pressure and a maximum temperature of 700°C. Later, this system was modified to withstand temperatures of 800°C, and designed for vacuum or gas atmosphere control and stress-free cooling. Specimen discs 3/4" diameter by 1/8" thick could be fabricated with this apparatus.

In addition, a second vacuum press was available for large specimen work (3" diameter, 1/2" thick). Its cavity was designed so that it could also be conveniently converted to press 1" diameter samples.

Materials:

The materials under discussion are, almost exclusively, fluorides. One chalcogenide system was investigated.

Initially, all fluorides were obtained, as such, from commercial sources. Later a co-precipitation process for preparing the materials was developed, which yielded purer and more homogeneous mixtures, whereupon, practically all starting materials were prepared at Bausch & Lomb Incorporated.

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[1] Bibliography, (15)
[2] Bibliography, (18)
[3] Bibliography, (15)

Gold tubing, platinum crucibles and boats, and iridium pots were used exclusively for reacting the fluorides. Silica tubes were used for the less emphasized chalcogenides.

III. METHODS

In all cases, the goal was to prepare homogeneous, monophasic, compositions over the maximum range of solid solution in a given system. After establishing the nature of the defect structure, efforts were made to hot-press polycrystalline specimens of varying composition for property study.

Crystal structure of the component fluorides, and the relative size and charge of the metal cations, were the primary considerations in designing systems most apt to yield the desired defect solid solution. Availability and cost of the materials were other factors.

In practice, the work consisted in preparing starting fluoride mixtures of the proper proportions and reacting small quantities to establish time-temperature-composition data for obtaining the proposed solid state reactions. Examination of the product established whether a desired defect type could be expected to obtain, as well as establishing a basis of compositions for further evaluation. Selected compositions were prepared in greater quantities, hot-pressed, and subjected to further study.

Experience with fluorides has shown them to be particularly susceptible to the adsorption of water. At elevated temperatures they hydrolyze readily and form oxyfluorides and oxides. For these reasons, starting materials had to be prepared free of water and stored in a desiccator. Also, during reaction, the mixtures were isolated from the furnace atmosphere to minimize the formation of secondary reaction products.

Preparation of Mixtures:

Mechanical mixing of dry powders and co-precipitation techniques were used in preparing the starting mixtures.

The former technique, used initially, involved weighing out the desired quantities of constituent fluorides--powders of -100 mesh size--and mechanically mixing in an agate mortar; followed by vibration in a Wig-L-Bug*.

Later, co-precipitation methods were used with excellent results. This method involved co-precipitating mixed nitrate solutions with concentrated HF acid solution, drying, and calcining under a partial $NH_3 \cdot HF$ atmosphere. This preparation process, including the subsequent high temperature reaction step, is described in detail in a previous annual report[1].

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* Trade name for a vibrator used commonly by dentists in preparing dental amalgam.

[1] Bibliography, (17)

High Temperature Reaction:

Several techniques were available for reacting the prepared mixtures at elevated temperatures to effect solid solution formation. The particular one used was determined by the quantity of product desired.

For the preliminary survey work, where microgram quantities were adequate, the mixtures were reacted in sealed gold tubes in the Marshall tube, or the Glo-bar furnace. The details of this technique have been reported in an earlier report[1].

In preparing greater quantities of the materials, it was found necessary to work at high temperatures under a protective atmosphere. The Glo-bar reaction furnace, described elsewhere, therefore was used to react batches of approximately 15 grams. Reaction involved suspending a platinum crucible--containing the material--within the hot zone of the fused silica tube. Teflon plugs on the tube, provided with gas fittings, enabled atmosphere control within the tube.

Finally, reaction of pound-lot batches was effected in an iridium pot in the Harper glass-melting furnace under a N_2 atmosphere.

Hot-Pressing:

In order to obtain fully dense, polycrystalline compacts for evaluation, the sample powders were hot-pressed using the equipment previously described. The technique, briefly, involved compacting a charge of powder into a mold which could be evacuated while hot. Upon establishing thermal equilibrium and fully evacuating of evolved gases, pressure was applied through a hydraulic ram. Optimum pressure-temperature conditions varied according to the material under study. The span of temperatures and pressures generally used was 450° - 650°C at 30,000 - 68,000 psi.

In addition, a few hot-pressings were attempted between 900°C and 1100°C. at 6,000 psi, in a system which had no provision for evacuation during pressing.

Attainment of the best results was, in practice, dependent upon the amount of material available for experimentation.

Evaluation:

After reaction, the appearance of the samples was noted to determine whether sintering took place and the relative degrees; or whether melting had occurred. Color changes and other distinguishing features were noted. The samples were then powdered and stored in small, numbered glass phials.

[1] Bibliography, (15)

The optical polarizing microscope was used extensively to examine materials for homogeneity and other optical characteristics. Usually, it was possible to determine whether the individual grains, as well as the compacts, were isotropic. Refractive indices were measured using oil immersion techniques. Dispersion staining techniques were used where applicable. Significant change of refractive index of materials reacted to homogeneity was one of the criteria used to demonstrate crystalline solubility, and hence, defect concentration where components were not of similar formal formula.

Powder X-ray techniques were relied upon to confirm homogeneity and obtain phase data and crystal structure. Changes in lattice parameters, plus the lack of X-ray detection of expected second phases, confirmed the occurrence of prepared defect materials.

Comparison of pycnometric densities versus densities calculated using parameters obtained from X-ray data formed the prima facie line of evidence used in categorizing the defect materials into the major groupings of net vacancies or net interstitials.

The correlation of radioluminescence to defect type and concentration was entirely qualitative. Comparison of colors of powdered samples exposed to gamma radiation was made visually immediately after removal from the source.

Other measurements on the hot pressed compacts included IR transmission, hardness, and electrical conductivity.

IV. EXPERIMENTS AND RESULTS

Description of the Experiments:

The following table lists the fluoride systems investigated, the type of defect expected, and the concentration range studied. Reactions, in general, were effected for 1/2 to 1 hour periods at temperatures from 700°C to 1300°C.

TABLE I

System	Defect Expected	Conc. Range Studied
MgF_2-NiF_2	Substitutional	10-90 mole % NiF_2
KF-MgF_2-NiF_2	Substitutional	{90 mole % $KMgF_3$ / 10 mole % NiF_2} = {90 mole % $KNiF_3$ / 10 mole % MgF_2}
$KMgF_3$-LiF	Anion vacancy	10-50 mole % LiF
$KMgF_3$-SbF_3	Cation vacancy or interstitial anion	
$KMgF_3$-AlF_3		
$KMgF_3$-InF_3		
$KMgF_3$-GaF_3		
$KMgF_3$-ScF_3	Cation vacancy or interstitial anion	10-40 mole % ScF_3
CaF_2-YF_3	Interstitial anion	0-80 mole % YF_3
CaF_2-$NaLaF_4$	Substitutional, half-breed	0-20 mole % $NaLaF_4$
NaF-YF_3-CaF_2	Interstitial anion and half-breed	0-40 mole % CaF_2
LaF_3-SrF_2	Interstitial cation or anion vacancy	0-40 mole % SrF_2

Description of the Results:

The following is a brief summary of the experimental results observed for each of the systems studied. More detailed experimental data is available in the annual reports[1].

MgF_2-NiF_2

MgF_2 and NiF_2 have the same rutile-type structure and both Ni^{2+} and Mg^{2+} have identical ionic radii (0.78 Å). Consequently, complete solid solubility between the end members to form a "substitutional" defect was expected.

Mechanically mixed samples of MgF_2 containing 10 mole % to 90 mole % NiF_2 were reacted in the temperature range 400°C to 1200°C. Between 400°C and 600°C, NiO forms and becomes more pronounced at the higher temperatures. Elimination of NiF_2 oxidation was never accomplished, even though the dried powders were reacted in vacuo and under dry nitrogen. Nonetheless, it was established that solid solutions form at temperatures exceeding 800°C. The refractive index of the solid solutions increased from 1.378 in pure MgF_2 to 1.568 in NiF_2; e.g. n of the 20 mole % NiF_2 ss = 1.406; n of the 90 mole % NiF_2 ss = 1.515.

NiF_2-MgF_2 mixtures, prepared by co-precipitation methods, appeared to be homogeneously mixed when dried at a low temperature on a steamplate. The NiF_2-rich compositions tended to oxidize when the drying temperature exceeded 200°C. The MgF_2-rich compositions were calcined in a dry nitrogen atmosphere at 400°C without apparent oxidation. Extensive oxidation, with corrosion of the retaining ring, occurred when attempts were made to hot-press the latter samples at 650°C. The specimens were, at best, translucent to visible light and exhibited infra red transmission to 9 μ.

Custom melts of two MgF_2-NiF_2 compositions, of 5-pound quantity, were contracted from a commercial supplier. These also, were badly oxidized.

Perovskite Structure Systems:

Perovskite was prepared from MgF_2 and $KF \cdot 2H_2O$. Complete reaction to $KMgF_3$ occurred between 500°C - 800°C. Above 300°C, both perovskite and MgF_2II (a phase reported unstable below 700°C[2]) exist. X-ray reflections were sharp and indicative of well-crystallized material.

[1] Bibliography, (15-18)
[2] Bibliography (1)

Compaction at 30,000 psi and 600°C-700°C, in metal retaining rings, yielded very dense, translucent specimens which, however, cracked extensively in the rings.

Single crystals of $KMgF_3$ were prepared from melts of $MgCl_2$, MgO, and KF·HF mixtures in platinum crucibles at 900°C. Well crystallized cubes, up to 1 mm on a side, were obtained. Use of heavy liquids indicated these crystals to be denser than reported in the literature. ASTM powder X-ray data cards report a density of 2.8 g/cc, while the sink-float method indicated a density of 3.15-3.20 g/cc.

Having found $KMgF_3$ rather easy to prepare--and highly stable--it was felt the $KMgF_3$ would be a good host structure for trivalent fluorides substitutions. Also, it was hoped that Ni^{2+} could be substituted into this system with a minimum of NiO formation.

Consequently, a cursory investigation was made of the perovskite systems $KMgF_3$-NiF_2, $KMgF_3$-LiF, $KMgF_3$-SbF_3, $KMgF_3$-AlF_3, $KMgF_3$-InF_3, $KMgF_3$-GaF_3, and $KMgF_3$-ScF_3. With the exception of the system $KMgF_3$-ScF_3, wherein a new phase was discovered and studied, an extensive investigation was not made of these systems. As stated earlier, detailed observations regarding these systems can be found in previous annual reports.

$KMgF_3$-ScF_3

The potential for extensive solubility of Sc^{3+} in $KMgF_3$ is enhanced by the fact that ScF_3 has essentially the perovskite structure, except for the missing large monovalent ion at the center of the unit cube. Furthermore, the unit cell dimensions of the two structures are essentially the same.

Four compositions of ScF_3 in $KMgF_3$, 10-40 mole % ScF_3, were reacted over the temperature range 700°C-1050°C for periods of 1/2 - 2 hours.

In all cases, some melting occurred between 900°C - 950°C. Also, the solidus in the system appears to be very flat over a wide composition range. Sintering was not very pronounced below 850°C, although solid state reaction was effective as low as 700°C. Reaction below the solidus, at 900°C, was quite complete after two hours. However, the most effective temperature for forming large crystals occurred above the solidus, at ca. 950°C, and required a time in excess of 1/2 hour.

Reaction invariably resulted in a combination of the phases $KMgF_3$, ScF_3, and a new tetragonal phase (X).

Optically, it was very difficult to distinguish between the three phases. ScF_3 and $KMgF_3$ are both isotropic with a refractive index very close to one another--ca. 1.404. The X-phase was found to be anisotropic and weakly birefringent, but with an index of refraction also very close to 1.404.

At concentrations up to 24.5 mole % ScF_3, cubic crystals predominate. The 40 mole % ScF_3 mixture, on the other hand, yielded well-formed prismatic crystals of the new phase, without the appearance of cubic crystals (although the presence of the perovskite phase is indicated by the X-ray pattern). Presumably then, a phase boundary exists somewhere between the $KMgF_3$ compositions containing 24.5 mole % ScF_3 and 40 mole % ScF_3.

On the high ScF_3 side of the boundary—above the solidus—the prismatic new phase is primary and large crystals grow from the melt. The perovskite phase, which was not recognizable under the microscope, is discernable in the X-ray patterns, and consequently must be in a finely divided state—perhaps as a result of rapid crystallization during quenching.

On the low ScF_3 side of the phase boundary, large primary cubes grow from the melt. Frequently, however, well-developed prismatic crystals were also observed. Possibly, an abnormal sub-solidus relationship exists which would account for this occurrence.

Anisotrophy of apparently cubic crystals was observed in the materials at the lower concentrations of ScF_3. This is suspected as being due to a degradation of cubic symmetry resulting from dissolution of ScF_3 in $KMgF_3$.

The omnipresence of the X-phase in the compositional range studied made it difficult to isolate a monophasic solid solution material for hot pressing studies. Since this phase appeared to have an extensive range of solid solubility, efforts were made to determine the composition of the phase and find if a range of complete solid solubility did indeed exist. Electron microprobe analysis of a sample containing well-developed prismatic needles together with $KMgF_3$ and ScF_3 (as shown by X-rays) to serve as standards was attempted. It was found that all these phases had appreciable amounts of K, Mg, and Sc and the variability was such as to preclude unambiguous determination from one grain. The complex phase suites observed from these reactions made it clear that a rather involved phase equilibrium study would be required to gain the desired knowledge. This complexity and the high cost of ScF_3 favored suspension of further work along this line.

A description and X-ray data of the new phase, $xKMgF_3 \cdot ySCF_3$, is given in Appendix, A.

CaF_2-YF_3

Of the materials expected to yield solid solutions containing interstitial defects, the system CaF_2-(YF_3) yielded the most encouraging results.

In this system, interstitial defects were created when F^- ions were "stuffed" into the lattice to maintain electrical neutrality as the higher valency Y^{3+} ions replaced the Ca^{2+} ions in the fluorite lattice. Proportional increases in the unit cell size, density, and refractive index were observed with increasing YF_3 content (Appendix, B).

Reactions of CaF_2-YF_3 mixtures containing up to 80 mole % of YF_3 were performed at temperatures up to 1300°C. Mechanically mixed samples, as well as co-precipitated samples, yielded homogeneous solid solutions at the higher temperatures. However, co-precipitation techniques appeared to yield a purer product.

Powder X-ray diffraction analysis and microscopic examination of the reacted materials indicated the existence of a single phase solid solution through the 60 mole % CaF_2-40 mole % YF_3 composition. The 60 mole % YF_3 composition was diphasic, as was the 80 mole % YF_3 sample. Incidentally, the 80 mole % YF_3 sample also indicated the presence of the $CaF_2 \cdot 4YF_3$ compound first reported by J. M. Short[1].

There were no indications of a superlattice although several weak reflections not commonly observed in the CaF_2 pattern were present in the XRD powder pattern of the cubic CaF_2-YF_3 solid solutions. These unreported reflections, occurring approximately at 2θ values of 77.1°, 58.2°, and 32.6°, were also observed in cubic $NaYF_4$. They were attributed to the substitution of Y^{3+} ions into Ca^{2+} ion positions in the crystal; the greater electron density of Y^{3+} causing an increased intensity of these reflections, normally too weak to be discernible.

Large batches were reacted at 1300°C under N_2 and quenched in water. The sintered-molten mass was milled in a high purity alumina jar and charge, which resulted in slight alumina contamination of the material.

Well-accreted, 1"-diameter polycrystalline compacts were hot-pressed at 650°C and 68,000 psi pressure. Density values of these samples compare favorably with the theoretical densities of a F^- interstitial model and are presented in the Appendix, B.

Constant dosages of gamma radiation produced high concentrations of color centers in the powdered solid solutions. Although quantitative measurements were not made, the color intensity was observed to increase with defect concentration, in the limited samples that were examined. Mechanically mixed powders of comparable composition which had not been reacted at high temperature did not display coloration, while co-precipitated compositions, also not reacted at high temperature, colored very slightly. This agrees with refractive index data, which also indicates some solid solution formation directly attributable to co-precipitation.

Hardness measurements were not made on sufficient samples to establish a reliable trend but nonetheless serve to give an idea of the approximate hardness of these materials. However, it is noteworthy that all the hot-pressed specimens in this series, including the pure CaF_2, indicated a greater hardness than that of a single crystal specimen of CaF_2.

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[1] Bibliography, (2)

The infra red transmitting properties of hot-pressed CaF_2-YF_3 and pure CaF_2 specimens were compared against each other and single crystal CaF_2. Other than a lowering of the per cent transmission, which is not necessarily due to the YF_3 in the host CaF_2, the solid solutions were very similar to the pure CaF_2. This type of scattering is commonly observed in materials which have not been pressed under optimum conditions. Several of these curves are included in the Appendix.

A summary of the physical properties of these materials is given in the Appendix, B.

NaF-YF_3-CaF_2

Initial efforts at preparing a "half-breed" defect material were made with the system CaF_2-$NaLaF_4$ and $NaYF_4$-CaF_2. Extensive oxidation of $NaLaF_4$ to form LaOF was observed when the reaction temperature approached 700°C. Consequently, the more stable system $NaYF_4$-CaF_2 was selected for study.

The system NaF-YF_3 is reported to contain two intermediate compounds, NaF·YF_3 and 5NaF·9YF_3, each existing in two polymorphic forms[1]. The NaF·YF_3 compound has the cubic fluorite structure at temperatures above 700°C and a hexagonal structure at lower temperatures. The 5NaF·9YF_3 compound has the cubic fluorite structure above 710°C. Between 710°C and 537°C, an ordered form is stable, while below 537°C, the compound decomposes to hexagonal NaF·YF_3 and YF_3.

With the end view of preparing NaF·YF_3-CaF_2 solid solutions, the system NaF-YF_3 was studied. Compositions in the range 60 mole % YF_3-40 mole % NaF to 40 mole % YF_3-60 mole % NaF were reacted over the temperature range 700°C-1100°C. The sodium-rich mixture invariably yielded a multiphase material believed to be predominantly NaF and Hex. $NaYF_4$, while a 1:1 composition yielded a mixture of the polymorphs—the hexagonal and cubic $NaYF_4$. A stable, homogeneous cubic solid solution was formed by the YF_3-rich mixture and consequently a composition in this region was chosen for subsequent reactions with CaF_2.

The cubic composition 3NaF·5YF_3 was selected and efforts were made to alter its structure through the purposeful substitution of CaF_2 into the lattice. Assuming the undistorted, fully disordered cubic structure to obtain, the 3NaF·5YF_3 solid solution contains interstitial F^- ion defects at an average of one per unit cell. This postulation was verified by comparing the apparent density of hot-pressed specimens with the calculated theoretical density for this model (see Appendix, C). Incorporation of the Ca^{2+} ion in increasing amounts resulted in a proportional dilution of the interstitial F^- ion stuffing.

[1] Bibliography (11)

At 20 mole % CaF_2 content, the average interstitial F^- ion defect content of the crystal was calculated to be 0.8 F^- ions per unit cell, as Ca^{2+} ion assumed the Na^+ and Y^{3+} ion positions. Related observed changes included contraction of the unit cell, decreases in density, and lowering of the refractive index.

Single phase solid solutions were obtained by reacting the co-precipi' compositions at 1250°C. under a nitrogen atmosphere and quenching in air. Slight solid solution was observed to occur at calcining temperatures.

X-ray diffraction analysis of the reacted powders at slow scanning speeds verified the fluorite cubic structure with no superstructure. Repeated measurement of the d-spacing between {111} planes indicated the expected lattice contraction.

Microscopic analysis revealed the solid solutions to be composed of very homogeneous, well-formed grains. Some contamination was apparent. Spectroscopic analysis indicated the presence of aluminum, presumably from the alumina mill.

When hot-pressed, excellent 1"-diameter compacts--well-accreted and translucent--were obtained at 650°C and 68,000 psi. A noticeable cloudy effect within the polycrystalline aggregates was apparent. Cracking of the compacts occurred and was somewhat alleviated by allowing the samples to cool to room temperature in the die before removal. Phase separation did not occur upon slow cooling in this manner.

Displacement methods were used to determine the density of the polycrystalline compacts. The results corresponded closely to the calculated theoretical values for an interstitial F^- defect solid solution (Appendix, C).

All the compositions within this system exhibited intense coloration upon exposure to constant dosages of ionizing radiation for periods up to 4 hours. Although the observations were strictly qualitative, the intensity appeared to be higher in the samples containing CaF_2 than in the pure $3NaF \cdot 5YF_3$ material.

No variation in hardness or infra red transmission with a change in defect concentration could be detected.

A summary of the physical properties of these materials is given in the Appendix, C. Infra red transmission curves also are included in the Appendix.

LaF_3-SrF_2

The phase LaF_3 gives its own mineral name, tysonite, to a family of compounds in which the laser industry has shown considerable interest recently. To our knowledge, no one has previously reported large defect concentration in the tysonite structure. In our study of the system LaF_3-SrF_2, where the

hexagonal LaF_3 is the host matrix, it was believed that ion for ion replacement of La^{3+} by Sr^{2+} could result in the creation of an anion vacancy defect system. Although lattice contraction and decreases in density and refractive index with increasing SrF_2 content could be expected, the linearity of such a change could not be predicted due to the differing crystal structure of the end members. For this same reason, complete solid solution was not to be expected.

Co-precipitated compositions in the range 0-40 mole % SrF_2 in LaF_3 were prepared and calcined at 500°C. for 1-1/2 hour periods. Higher temperatures were not used because of the tendency of the LaF_3 to oxidize.

X-ray diffraction powder analysis and refractive index measurements established solid solution formation between 10-15 mole % SrF_2 in LaF_3. Furthermore, it was observed that extended calcination at 500°C resulted in partial exsolution of the dissolved SrF_2 phase. Conceivably, solid solution may be increased with a lowering of the calcining temperature and/or time. It is noteworthy that solid solutions could only be prepared by co-precipitation techniques. Mechanically mixed fluoride powders, of similar composition, did not form solid solutions when reacted under the same conditions.

It should be noted that the decrease in the lattice parameters of LaF_3 which occurred with increasing SrF_2 content was almost imperceptible. Theoretical densities were calculated from these parameters for an anion vacancy model and an interstitial cation model. Comparison with the apparent density of hot-pressed samples verified a predominantly anion vacancy defect model (Appendix, D). However, the fact that the apparent density was slightly higher than the theoretical density for an anion vacancy model, coupled with the almost imperceptible lattice contraction observed, also suggests the presence of some interstitial cation defects.

Hot pressing at 650°C and 68,000 psi pressure yielded excellent 1" diameter specimens. In the case of the 90 mole % LaF_3-10 mole % SrF_2 solid solution, these were well-accreted and transparent. General cloudiness of the 20 mole % SrF_2 samples was partially attributed to light scattering by the undissolved SrF_2 phase.

Infra red transmission out to 10 μ (see Appendix) was observed without any changes due to SrF_2 addition.

No coloration was observed upon exposure to gamma radiation. One would have expected to observe enhanced sensitivity to coloration because of the electron trap potential of the defect solid solutions; i.e., both anion vacancies and possibly also interstitial cations would have constituted direct traps for electrons. This occurrence, which has been observed in other systems having similar defects[1], has been attributed to the F-centers having maximum absorption outside the visible range.

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[1] Bibliography (19)

Of major significance were the unusual electrical properties displayed by the LaF_3-SrF_2 solid solutions. Whereas the other fluoride systems had indicated resistivities on the order of $>> 1 \times 10^{10}$ ohm-cm, resistivities of hot-pressed defective specimens in this system were recorded much lower--$\sim 1 \times 10^5$ ohm-cm. At first, these solid solutions were thought to be semi-conductors. However, further examination indicated them to be ionic conductors. It may be concluded that the current carriers are anions moving in the vacant ionic sites.

A summary of the physical properties of these solid solutions is given in the Appendix, D.

V. CONCLUSIONS

Although the survey work provided extensive data substantiating the existence of the proposed defects in significant concentrations, ideally straight-forward reactions were not readily accomplished.

Excessive hydrolysis or oxidation at elevated temperatures and difficulty in achieving single phase solid solutions in pound quantities were two of the major complications. In the cases where these complications and sundry minor ones were overcome--viz., the systems CaF_2-YF_3, NaF-YF_3-CaF_2, and LaF_3-SrF_2--the results, we hope, will prove useful.

To obtain optimum polycrystalline compacts, the defect fluorides must be homogeneous, monophasic solid solutions before hot-pressing. To achieve this, assuming the component fluorides are compatible with regard to solid solution formation, the following must be accomplished:

(a) complete and intimate mixing of the component fluorides prior to reaction;

(b) exact control of the time-temperature conditions required for solid solution; and,

(c) maintaining an oxygen-free and water-free system during reaction.

Co-precipitation methods of preparation were found to yield a homogeneous, reproducible starting mixture, and in some cases, promoted a substantial degree of solid solution formation without the need of high temperatures.

With the exception of the system LaF_3-SrF_2, high temperatures, generally above the solidus, were found necessary to achieve the formation of complete solid solution.

The presence of water, either free or of hydration, plays a significant roll in the formation of phases, and usually complicates matters. Thermal hydrolysis of fluorides to form oxide and HF, or oxyfluorides, is a common problem which was partially controlled through careful drying techniques and reacting under dry nitrogen. In some cases, notably the systems involving NiF_2, the problem proved insurmountable.

Of necessity, furthermore, Teflon, polyethylene, and noble metal reaction vessels must be used exclusively for preparing these materials.

Polycrystalline compacts were hot-pressed at 68,000 psi and 650°C to $> 99\%$ of theoretical density. The specimens, generally well-accreted, ranged from translucent to transparent in appearance. Extensive cracking

of the specimens invariably resulted due to the differences in the thermal expansion characteristics of the defect fluorides and the retaining ring material. This was somewhat alleviated by designing a die cavity conducive to stress-free cooling and by using slow cooling techniques. Phase separation was not observed due to slow cooling.

Great variations in the refractive index and density of a crystalline material were observed with increased defect concentration. However, no significant influence on infra red transmitting properties was apparent.

Solid solutions of SrF_2 in the hexagonal tysonite exhibited ionic conduction considerably higher than the pure tysonite and other type defect models. Since the defect nature of these solid solutions has been established as predominantly anion vacancies; presumably, anions serve as the current carriers.

VI. SUMMARY AND RECOMMENDATIONS

The research conducted under this contract has followed rather closely the rationale outlined in the proposal.

Four out of about a half dozen main structure-types have received attention as the host lattice: fluorite (typified by CaF_2), perovskite (typified by $KMgF_3$), tysonite (typified by LaF_3), and rutile (typified by MgF_2).

Half-breed and interstitial-anion fluorite phases with controlled defect content have been prepared in large sample sizes in a scale-up operation and hot-pressed blanks prepared and studied. Both substitutional and anion vacant perovskites and substituted rutiles have been synthesized but scale-up was not attempted for various reasons.

Among the physical property measurements, unit cell measurements by X-ray diffraction, density, and optical characteristics have received the most attention. These are, of course, also the most important for describing the defect nature of materials; although the mechanical, electrical and other properties remain of greater interest for applications.

Although the investigation was not as extensive as had been originally planned, the results of the study verified many of the predictions outlined. It has been demonstrated that desired defects can be designed into a structure to a substantial degree, that they influence certain properties and not others, and more importantly, that one can predict and fabricate materials having desired properties.

The success achieved in hot-pressing these defect fluorides should help expand the field of available IR optical materials, and the discovery of increased ionic conductivity in the defective tysonite structure offers new avenues of investigation for special electronic applications.

A significant new contribution to the literature was the discovery of extensive defect concentration in the tysonite structure and the establishment of the defect model as predominantly anion vacancies. Of academic interest, also, was the discovery of a new phase in the system $KMgF_3$-ScF_3.

The results of this study also have enabled us to discern to some extent both the most interesting lines of future research and also those which are most likely to succeed.

Hot-pressing as a new technology is probably the most important single advance in ceramic processing of the last several decades (excluding here the new glass-ceramic processes). The questions that have been

answered as a result of this study pertain largely to the range of materials which can be utilized, and the extent of control which can be exercised on desirable properties.

It appears that the pressure-temperature-time parameters are not affected in a major way by gross changes of defect-type and/or stoichiometry. However, the control of the chemistry, and the process (chiefly the vacuum) require considerable empirical development for each individual case. Once that is worked out for a particular phase, it is applicable to a family of materials based on the phase.

The areas in which hot pressing should immediately be exploited further as a ceramic processing tool are those in which:

(a) fine ultimate grain size,

(b) theoretical density (= zero porosity), and

(c) reproducibility,

are necessary or desirable.

Clearly the classes of uses to which these materials are put include:

(a) optical transmission, reflection, etc.;

(b) high strength application; and

(c) special electronic applications where the fine grain size is essential.

A P P E N D I C E S

A. Description of the Phase, $xKMgF_3 \cdot yScF_3$

Crystals: Acicular, prismatic, colorless. Weakly birefringent but thick crystals show up well between crossed Nicols. Crystals are length fast and show parallel extinction. Uniaxial, positive; tetragonal n = 1.404 ∓ 0.002.

X-ray: A single crystal Weissenberg X-ray diffraction photograph was made and interpreted by Tem-Pres, Inc. The specimen was taken from a 60 mole % $KMgF_3$-40 mole % ScF_3 composition. The unit cell dimensions were c = 4.0 Å, a = 17.7 Å.

Radiation: Cu Kα, = 1.5418 Å

2	d (Å)	I/I_u
* 25.36	3.512	80
* 27.36	3.266	40
28.14	3.171	12
* 29.05	3.074	100
30.02	2.977	20
34.03	2.634	5
36.22	2.480	5
* 36.95	2.433	20
38.26	2.352	20
40.60	2.222	5
* 41.55	2.173	80
42.85	2.110	15
* 48.18	1.890	30
48.82	1.865	5
51.58	1.772	5
52.90	1.731	15
53.70	1.707	12
55.08	1.667	12

* Indicates distinctive lines.

B. Physical Properties of Solid Solutions in the System CaF_2-YF_3

Composition	CaF_2	$9CaF_2:1YF_3$	$8CaF_2:2YF_3$	$7CaF_2:3YF_3$
Calculated density	3.18	3.42	3.63	3.88
Apparent density	3.17	3.3 * 3.4	3.6	- -
Refractive index	1.434	1.45	1.47	1.48
a(Å)	5.464	5.485	5.514	5.523
Hardness, K_{100}	209 ** 161	202	361	- -
Resistivity (ohm-cm.)	$\gg 1 \times 10^{10}$	$\gg 1 \times 10^{10}$	$\gg 1 \times 10^{10}$	- -
IR transmission limit	11 μ ** 11 μ	10 μ	- -	- -
Coloration by gamma radiation	sky-blue	yellow-orange	deep yellow-orange	- -

* hot-pressed at 1150°C and 4,000 psi

** single crystal specimen

C. Physical Properties of Solid Solutions in the System $NaF-YF_3-CaF_2$

Composition	$3NaF \cdot 5YF_3$	$9(3NaF \cdot 5YF_3):1CaF_2$	$8(3NaF \cdot 5YF_3):2CaF_2$	$6(3NaF \cdot 5YF_3):4CaF_2$
Calculated density	4.24	4.14	4.03	3.85
Apparent density	4.2	4.1	4.0	- -
Refractive index	1.475	1.465	1.465	1.444
a(Å)	5.514	5.504	5.502	5.479
Hardness, K_{100}	398	395	400	- -
Resistivity (ohm-cm.)	$\gg 1 \times 10^{10}$	$\gg 1 \times 10^{10}$	$\gg 1 \times 10^{10}$	- -
IR transmission limit	10 μ	10 μ	10 μ	- -
Coloration by gamma radiation	Deep yellow-orange	Deep yellow-orange	Deep yellow-orange *	- -

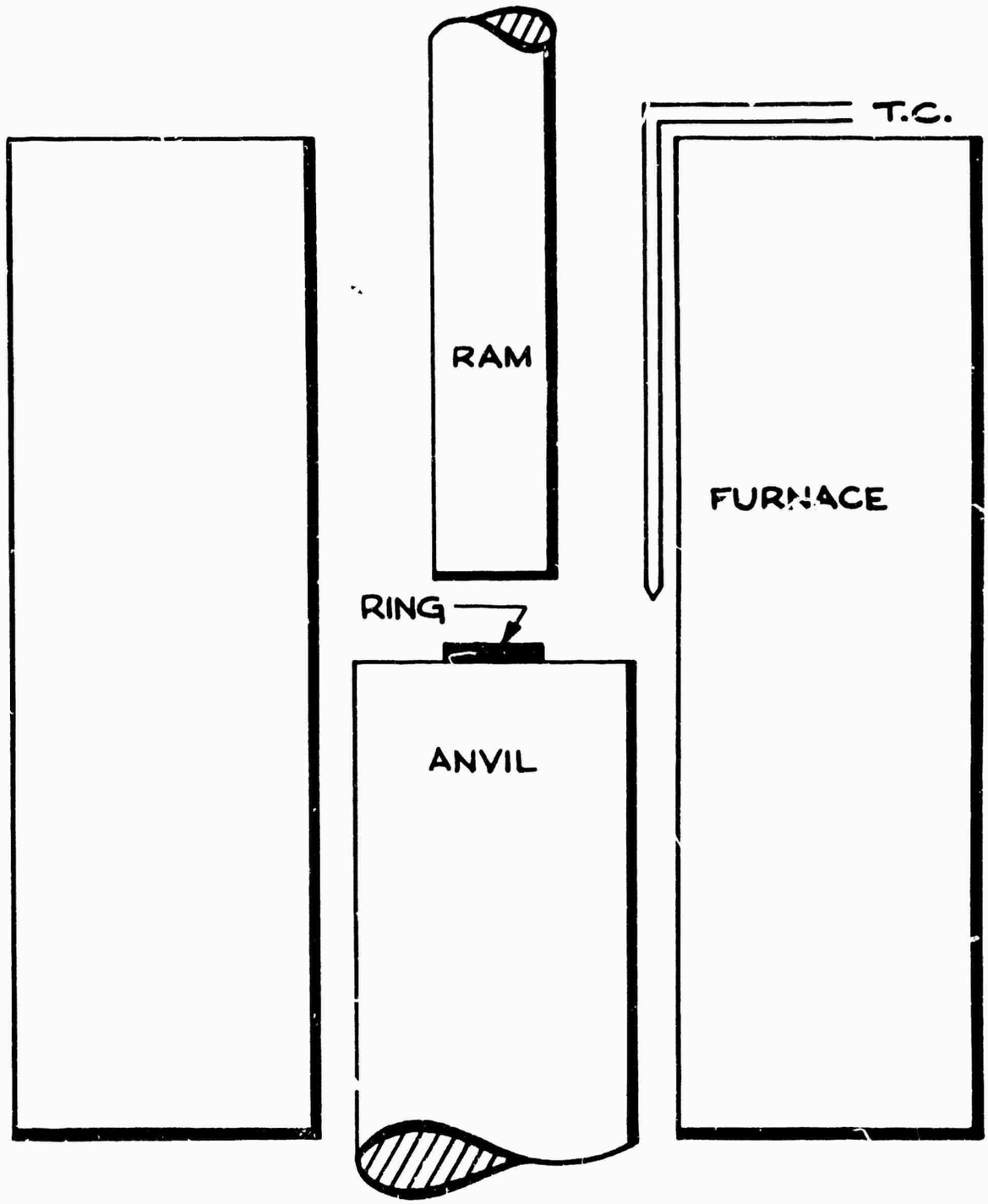
* more intense than the samples containing 0 and 10 mole % CaF_2

D. Physical Properties of Solid Solutions in the System LaF_3-SrF_2

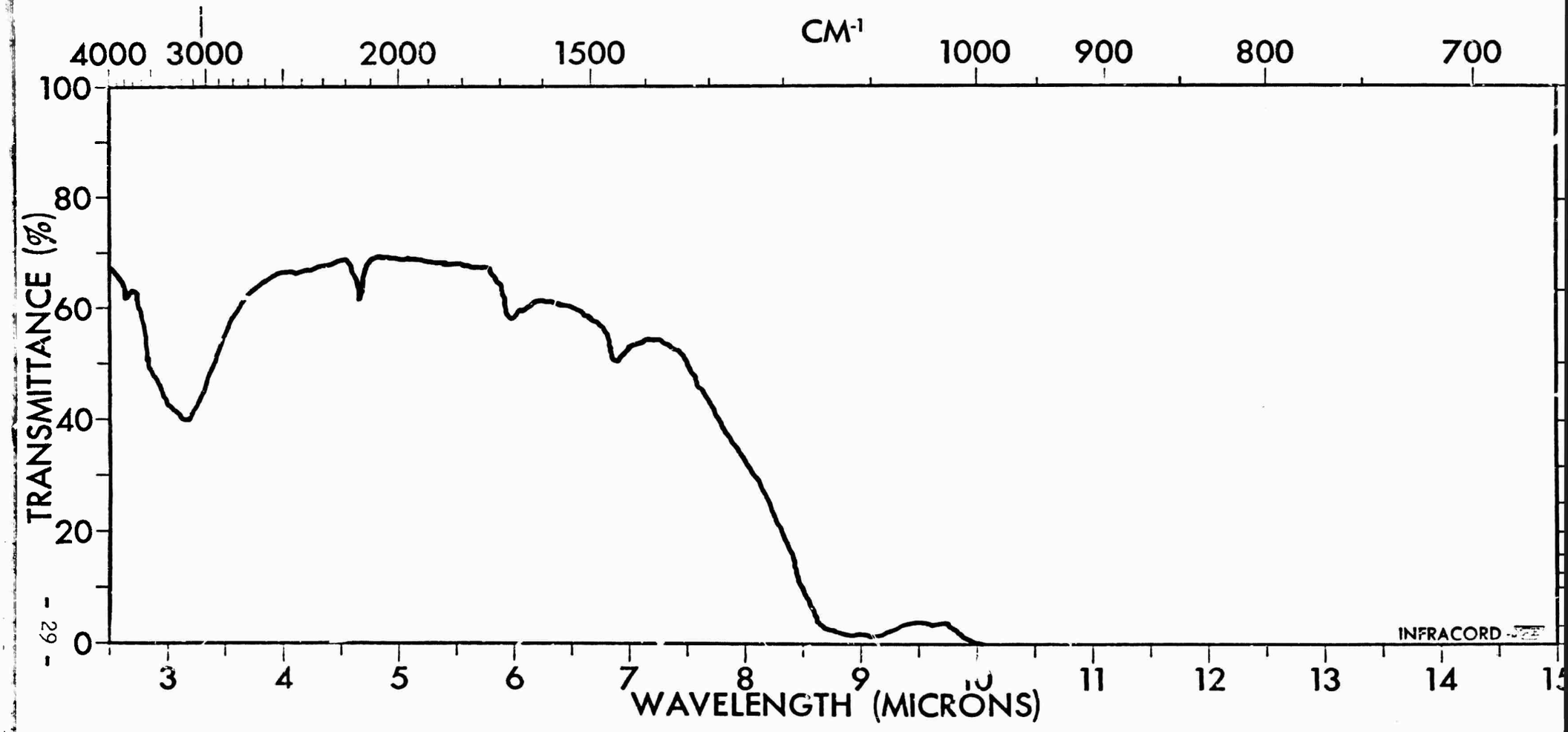
Composition	LaF_3	$9LaF_3$:$1SrF_2$	$8.5LaF_3$:$1.5SrF_2$	$8LaF_3$:$2SrF_2$
Calculated density for:	5.-			
(a) interstitial cation model		5.909	5.915	5.936
(b) anion vacancy model		5.712	5.620	5.540
Apparent density (g/cc)	5.92	5.73	- -	5.60
Refractive index	1.594	1.574	1.566	1.566
Hardness, K_{100}	438	409	- -	446
* Resistivity (ohm-cm,) at 1 Kc	$\geq 1 \times 10^9$	$\sim 9 \times 10^4$	- -	$\sim 9 \times 10^4$
IR transmission limit	11 μ	11 μ	- -	- -
Coloration by gamma radiation	Lt. beige	Colorless	- -	Colorless

* rough approximations

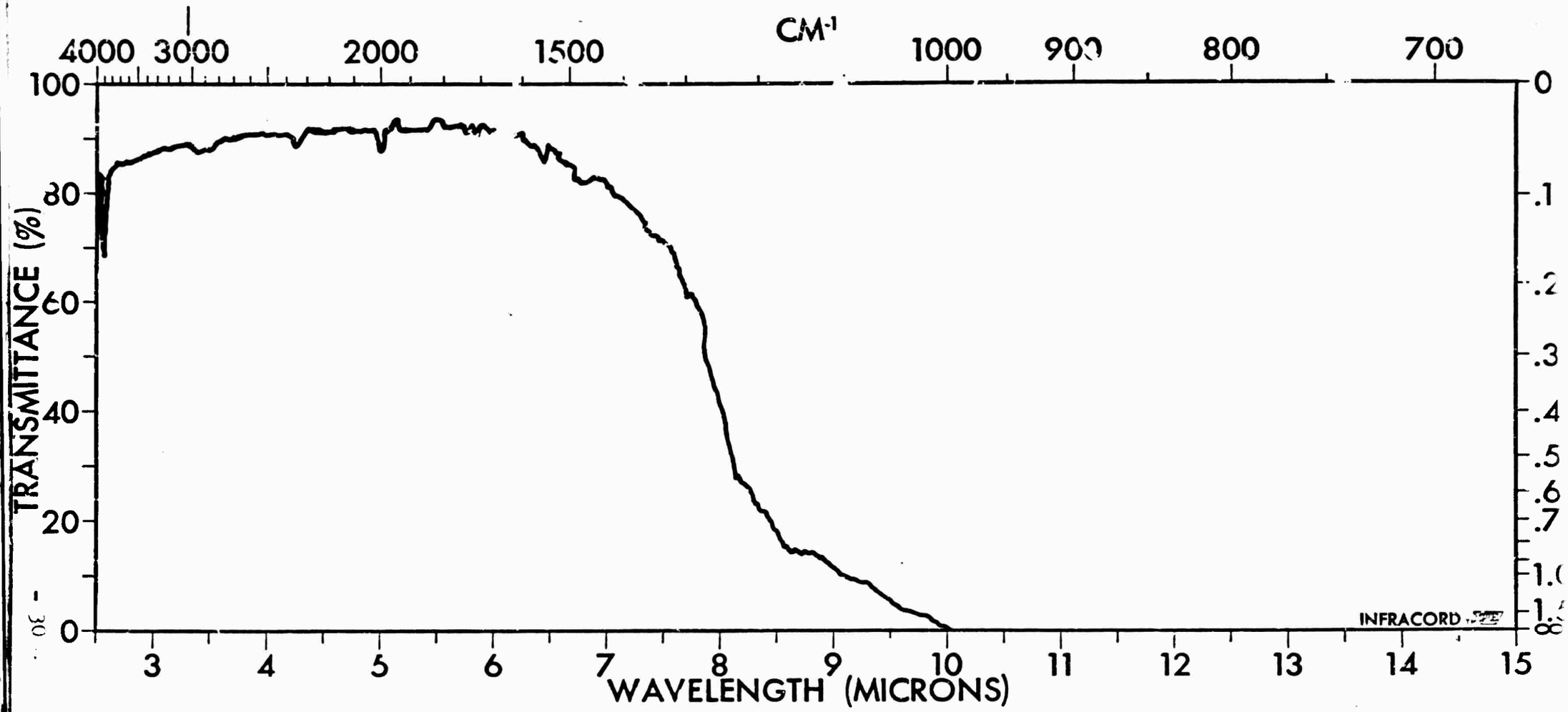
F HOT PRESS APPARATUS



F. Infrared Transmittance of Hot-Pressed Specimens



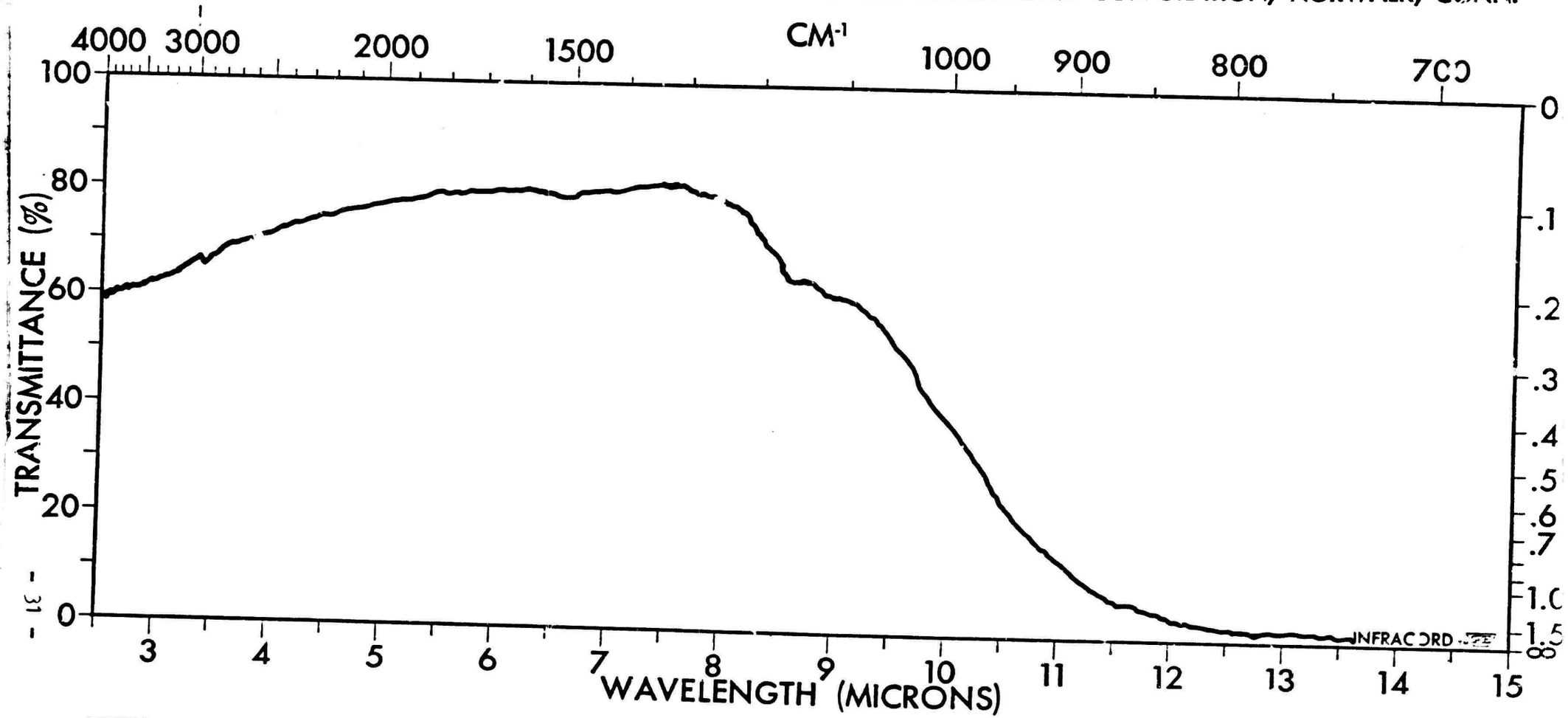
SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
$KMgF_3$	PURITY	2.	
	PHASE	DATE	
	THICKNESS 3.9 mm.	OPERATOR	



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
MgF_2	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2 mm.	OPERATOR	

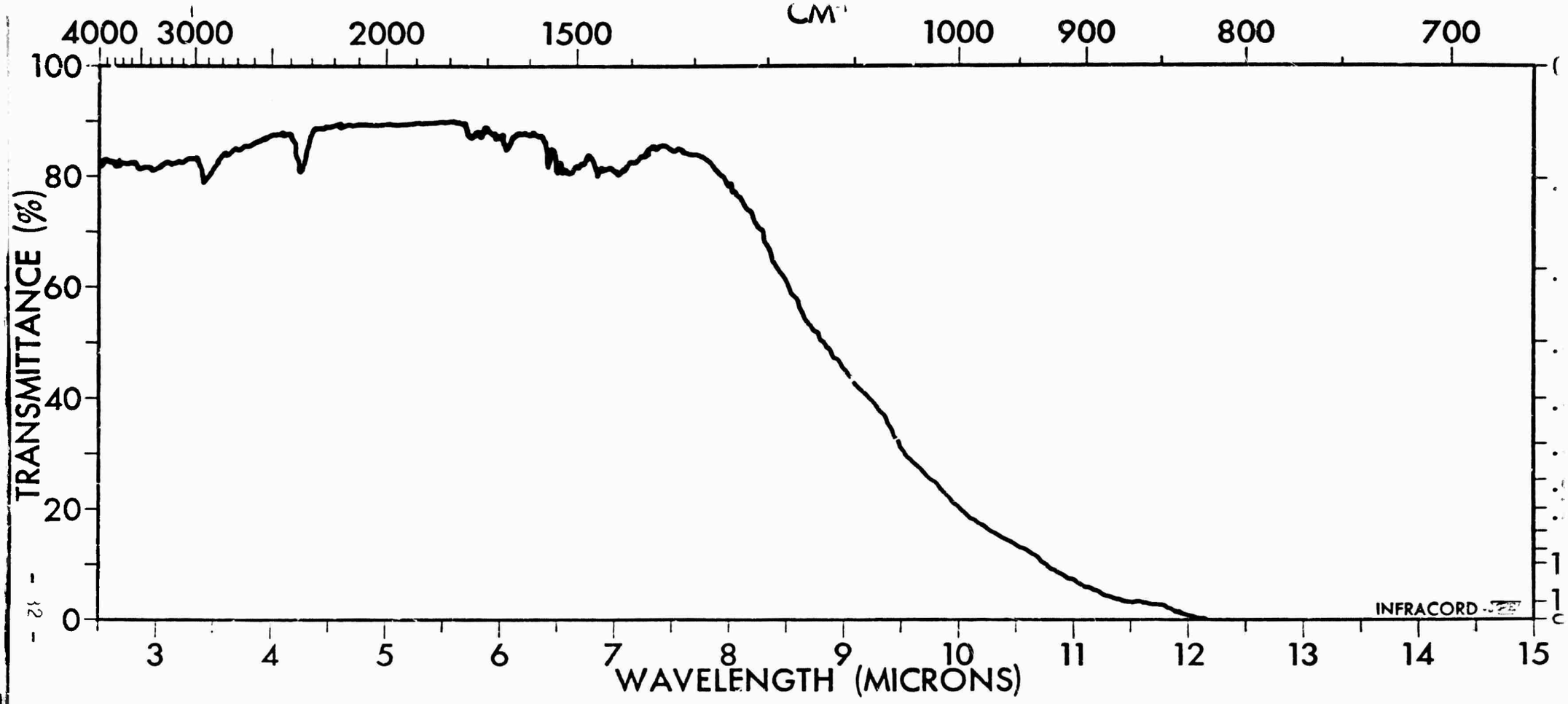
SAMPLE

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
Single Crystal CaF_2	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SPECTRUM NO. SAMPLE

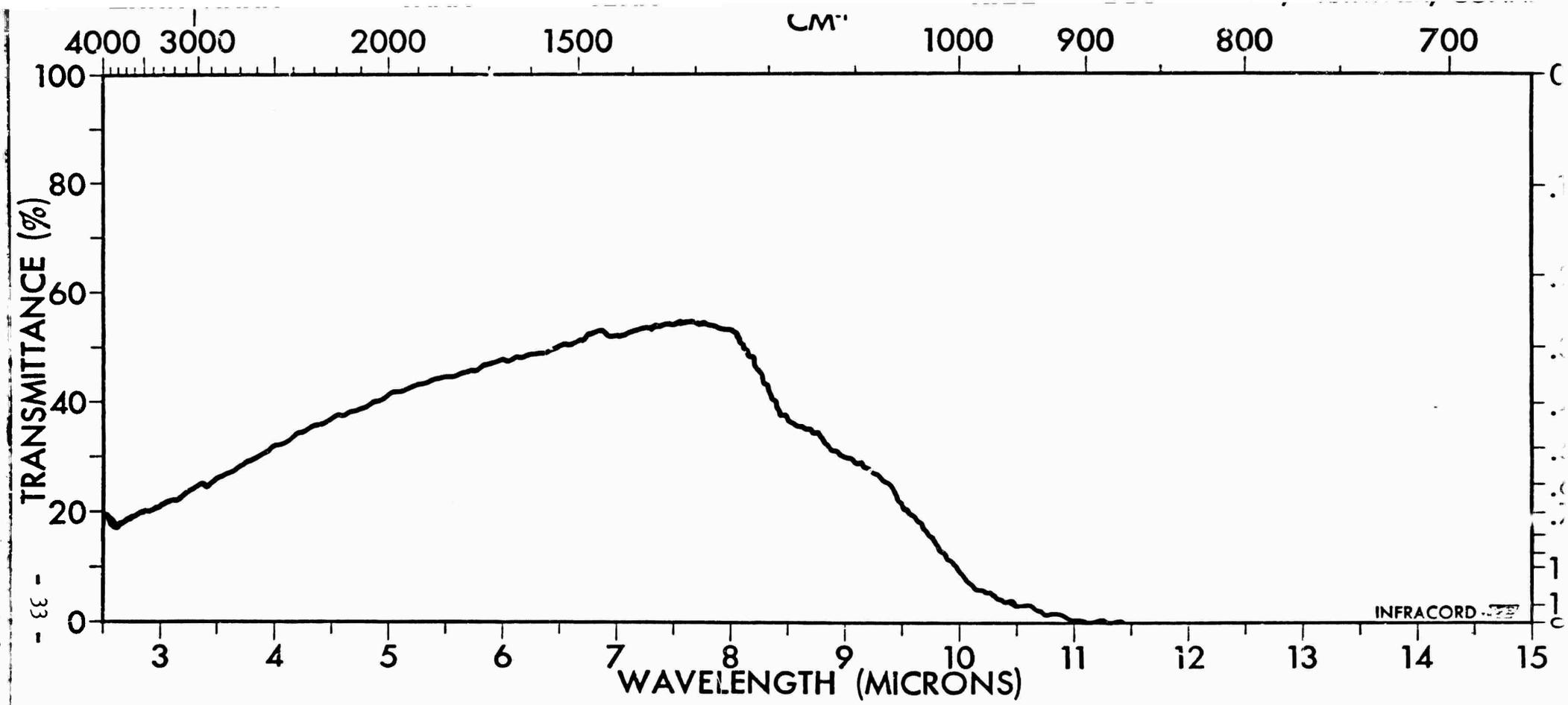


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
B+L CaF_2	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

PART NO. 137-1284

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
9 CaF_2 : 1 YF_3 ss.	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

PART NO. 137-1284

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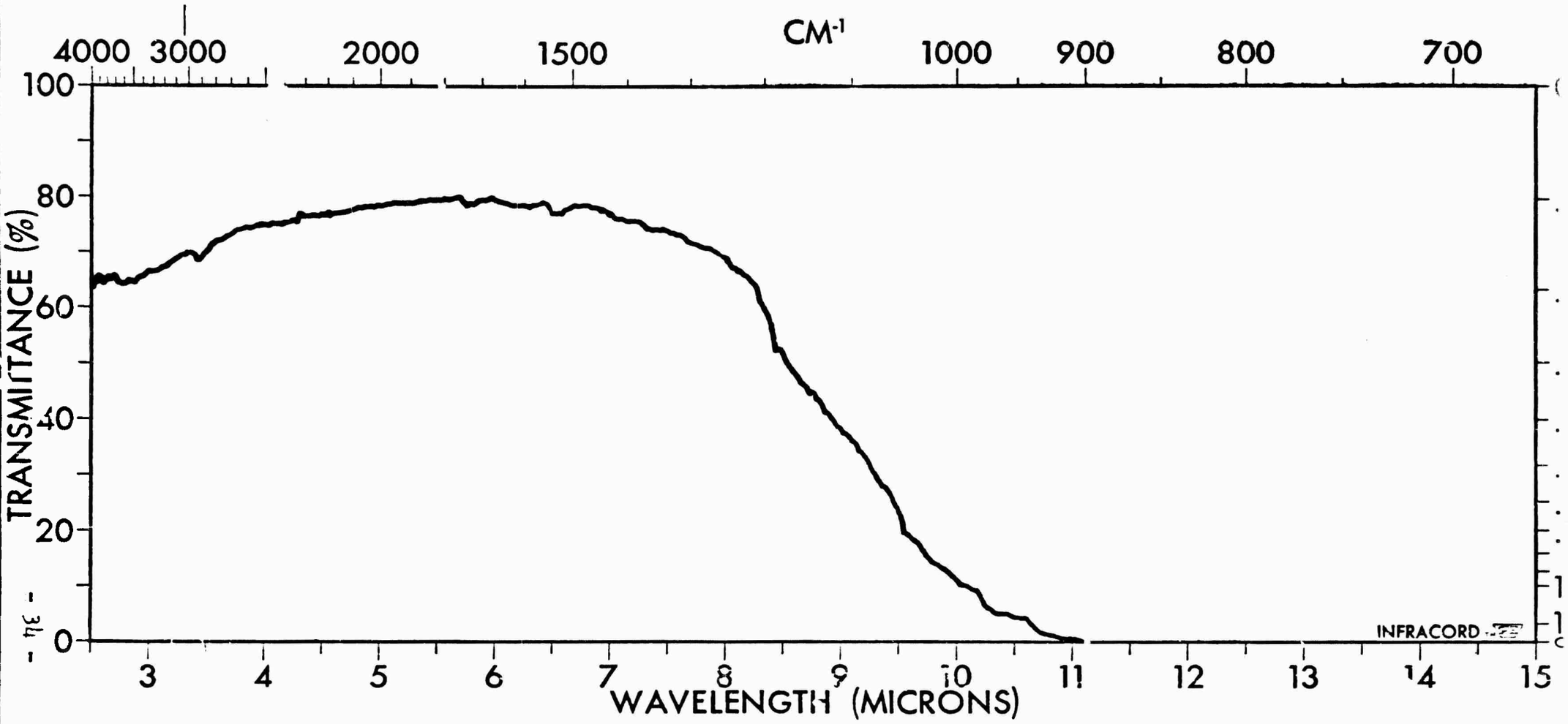

SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
3 NaF·5 YF_3 ss.	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

PART NO. 137-1284

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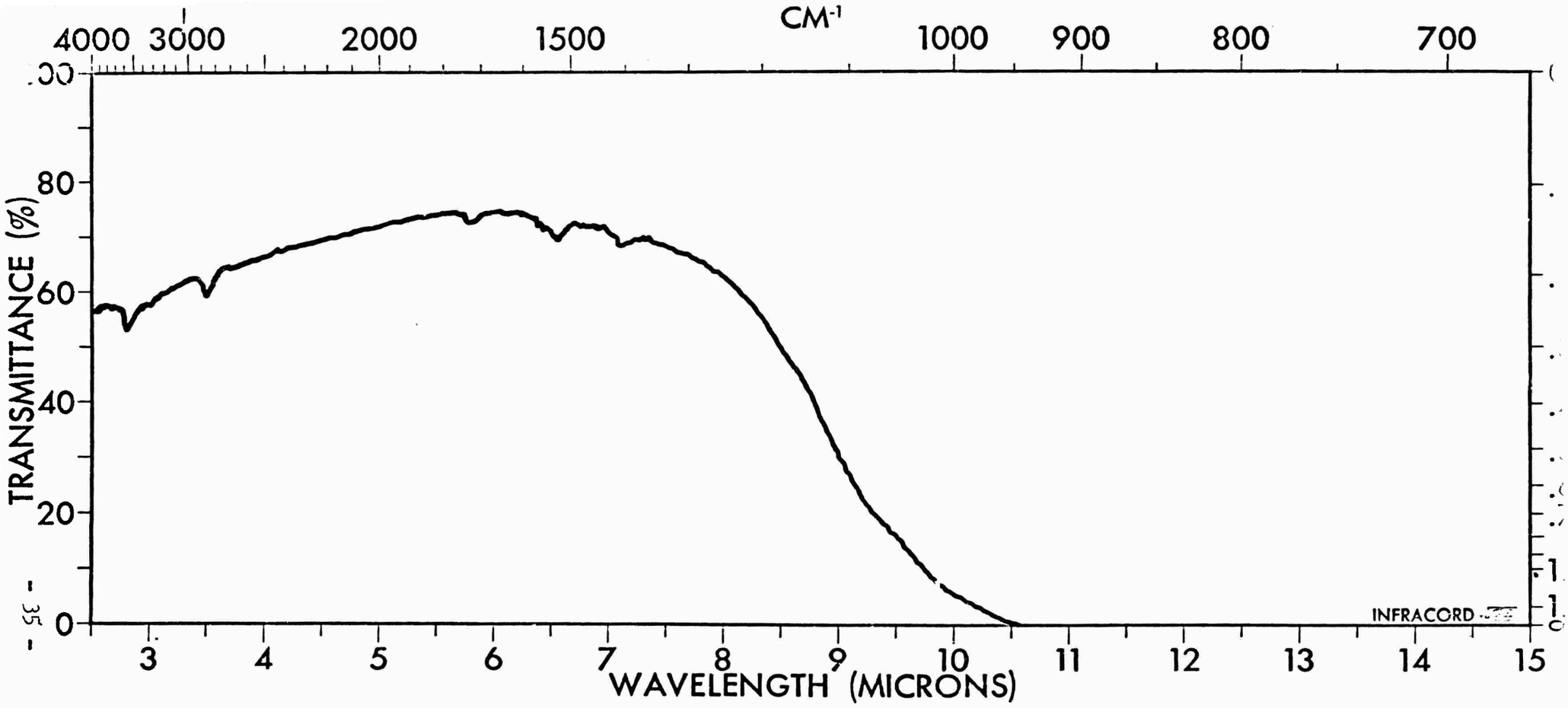
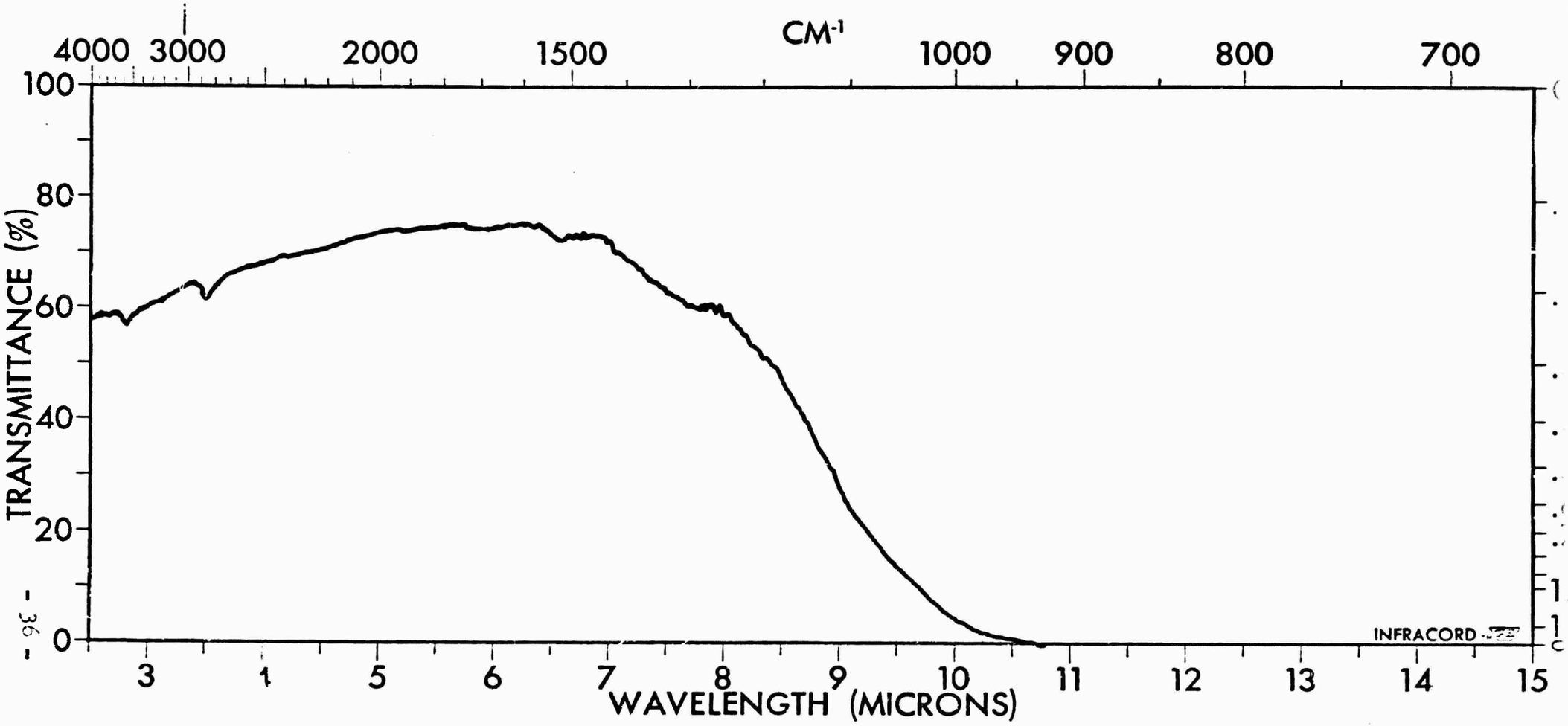


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
9(3NaF·5YF$_3$):1CaF$_2$ ss	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm	OPERATOR	

SAMPLE

PART NO. 137-1284

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

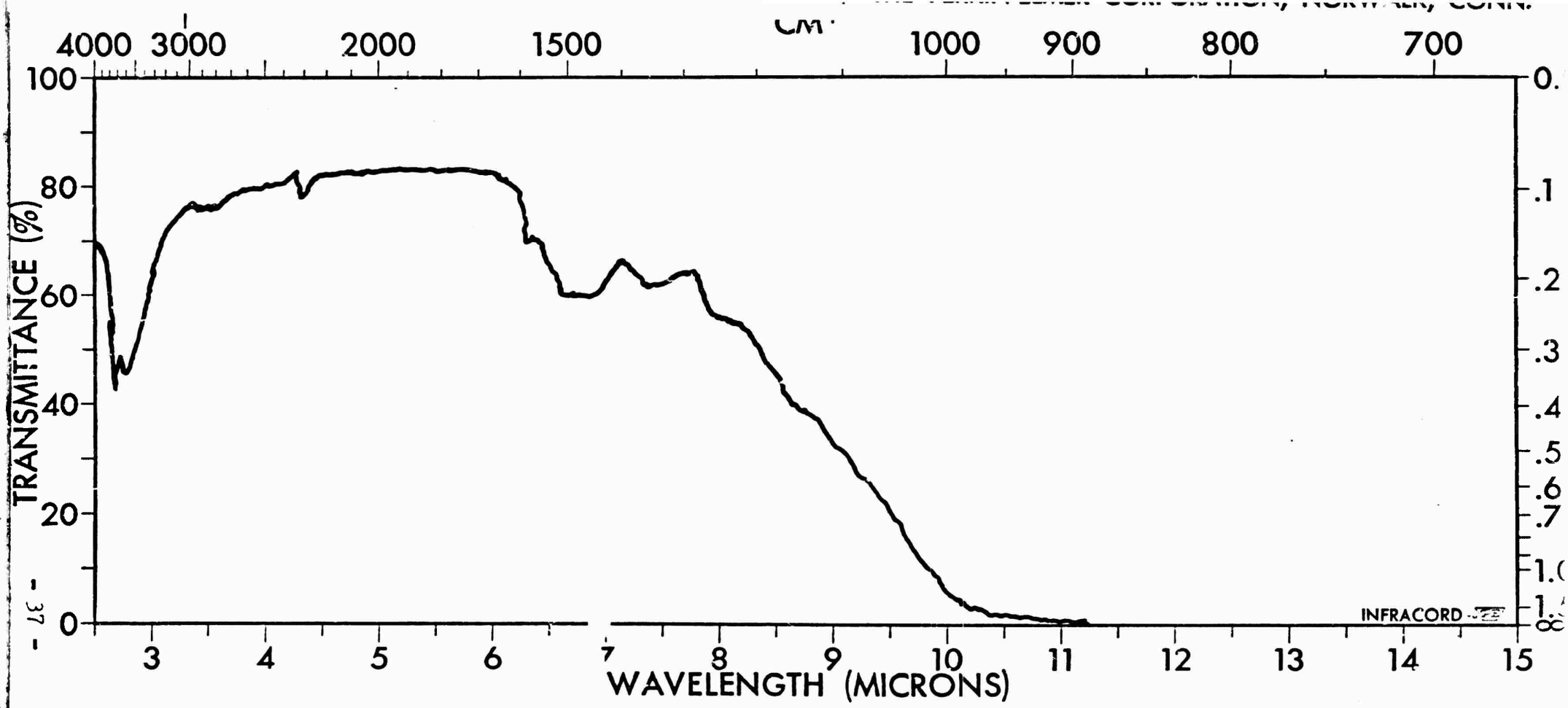


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
$8(3NaF \cdot 5YF_3) : 2CaF_2$	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

PART NO. 137-1284

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

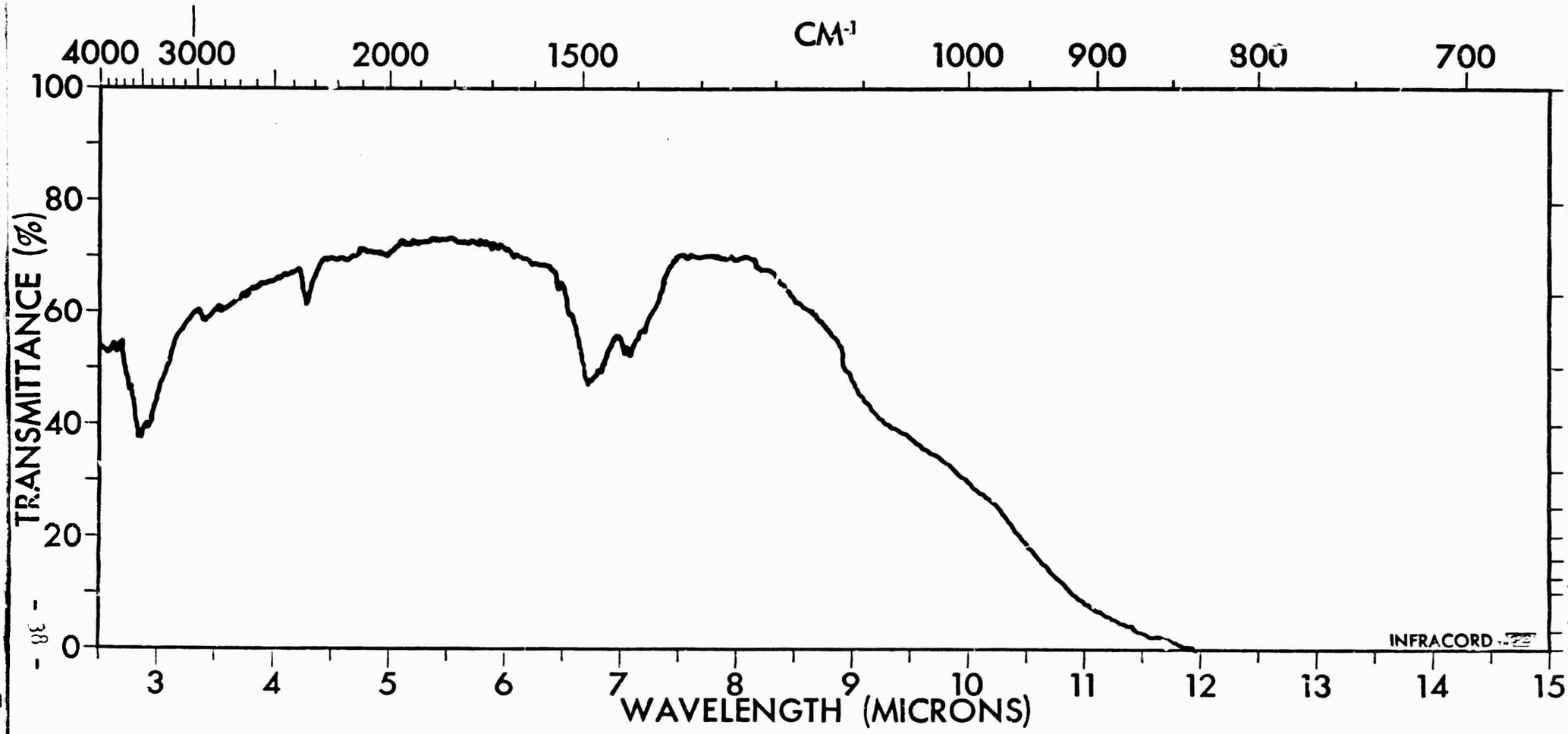


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
YF_3	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

PART NO. 137-1284

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.

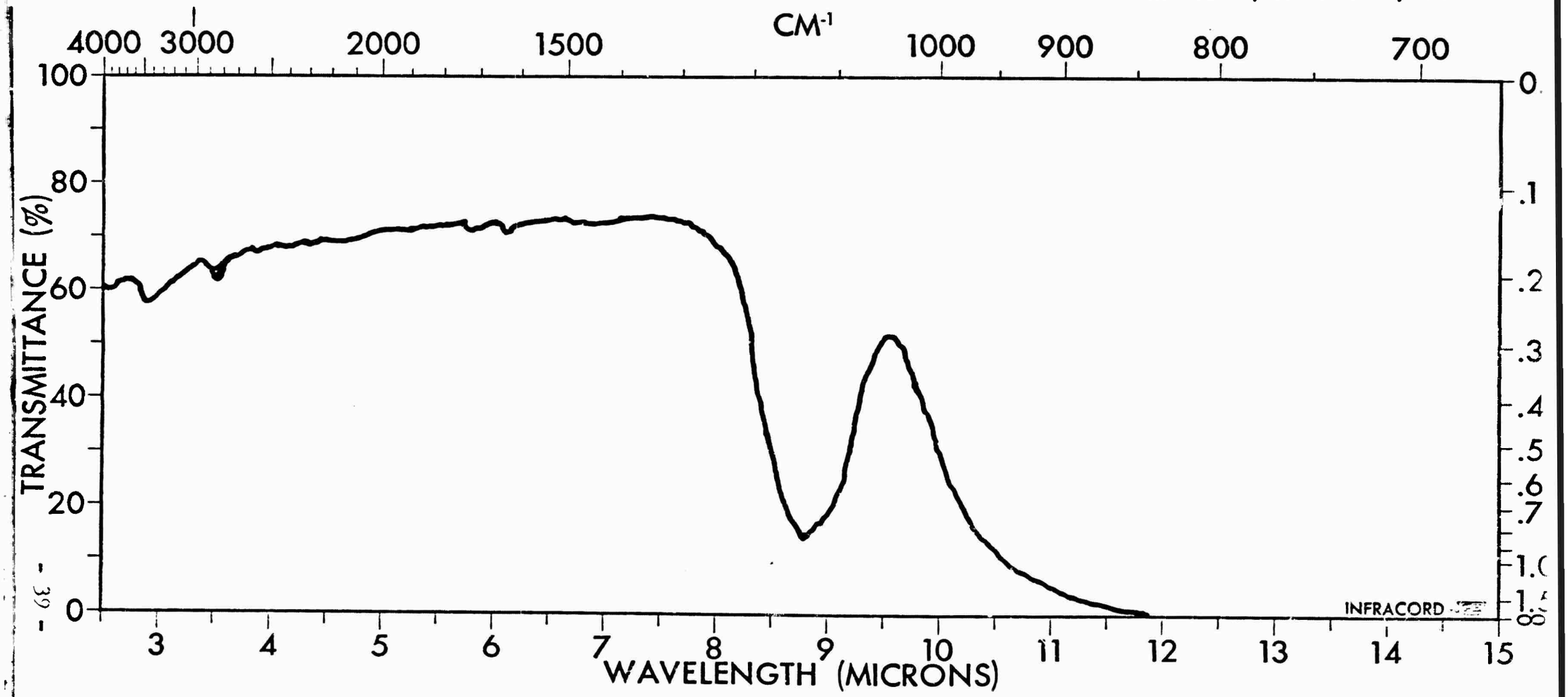


SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
LaF_3	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

PART NO. 137-1284

THE PERKIN-ELMER CORPORATION, NORWALK, CONN.



SPECTRUM NO.	ORIGIN	LEGEND	REMARKS
SAMPLE		1.	
9 LaF_3 : 1 SrF_2 ss.	PURITY	2.	
	PHASE	DATE	
	THICKNESS 2-3 mm.	OPERATOR	

SAMPLE

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